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Revision of the international calibration scale for CO2-in-air: WMO-X2005.

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The fifteen Primary Standards that define the current WMO Mole Fraction Scale for CO2-in-Air have been in existence since early 1991. They became the basis of the WMO Scale during the WMO CO2 Experts meeting in 1995. The first calibrations of these cylinders were carried out by the Scripps Institution of Oceanography, the WMO Central Calibration Laboratory (CCL) until 1995. CMDL has until now carried out six manometric calibration episodes of the Primaries starting in 1996. During each such calibration episode the CO2 mole fraction in dry air of each Primary was determined three or more times. The absolute uncertainty of the CMDL calibrations is 0.068 (one sigma). The repeatability (standard deviation of repeated individual measurements of each cylinder) of the calibrations has improved over time from 0.12 micromol/mol to 0.04 micromol/mol. The average of all cylinders during each episode varies between episodes with a standard deviation of 0.04 micromol/mol, which suggests small systematic variations of procedure between episodes, but not a trend. The "null" hypothesis, namely that there has been no drift of the mole fraction, cannot be rejected for any of the Primaries with the statistics we have. Therefore, we assume that there has been no drift until now, and the assigned value for each primary is the average obtained for that cylinder during all CMDL calibration episodes.

The above does not imply that the defined WMO Scale has not drifted. The early assigned values of the Primaries were based on infrared calibrations by Scripps against the WMO Scale as maintained by them. From 1996 through the fall of 2001 they were determined both by Scripps and CMDL calibrations. After the latter date the assigned values were determined exclusively by CMDL manometric calibrations. The average of all assigned values to the Primaries increased by 0.16 micromol/mol from 1996 to 2005. In the ambient range of 345-415 micromol/mol, the average increased by 0.14 micromol/mol. From late 2001 until 2005 the average of all assigned values of the Primaries has decreased by 0.01 micromol/mol for both the full range and the restricted (ambient) range.

In June 2002 CMDL received revised numbers from Scripps for the four calibrations by them of our fifteen WMO Primaries that they had carried out from 1991 to 1999. Their revised scale was called X99A. The average of all Scripps calibrations of all of our Primaries on the X99A scale was 0.06 micromol/mol higher than the average of all

CMDL calibrations, while their average in the ambient range (345-415) was 0.02 micromol/mol higher than ours.

In addition, in 2005 we carried out, at the request of Y. Tohjima of the National Institute of Environmental Studies (NIES), calibrations of five new gravimetric standards (approx. 350 and 390 micromol/mol) made by one-step dilution by Japan Fine Products Company. The average of the NIES values was lower than CMDL's by 0.004 micromol/mol, and the standard deviation of the individual comparisons was 0.02 micromol/mol.

Based on the assumption that the fifteen WMO Primaries have been stable, we have re-assigned a constant value (the average of the measured values during the six CMDL calibration episodes) to each of them going back to 1994. We call this revised scale WMO-X2005. The assignments of the CMDL secondary standards, that derive their values directly from the Primaries by repeated infrared comparative measurements, have also been recalculated going back to 1994. All other calibrations of CO2 reference gas cylinders were then recalculated based on the revised values of the secondaries. With few exceptions the other calibrations have always been done relative to the secondary standards. All laboratories and individuals for whom we have calibrated CO2 standards in the past will be able to read the previous and the newly revised values of their reference gases from the CMDL website (www.cmdl.noaa.gov/ccgg/refgases/) upon entering the cylinder number of the reference gases, or they may contact Mr. Duane Kitzis at CMDL.